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Partial phase transitions in magnetocaloric material MnFe(P,As)

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Introduction

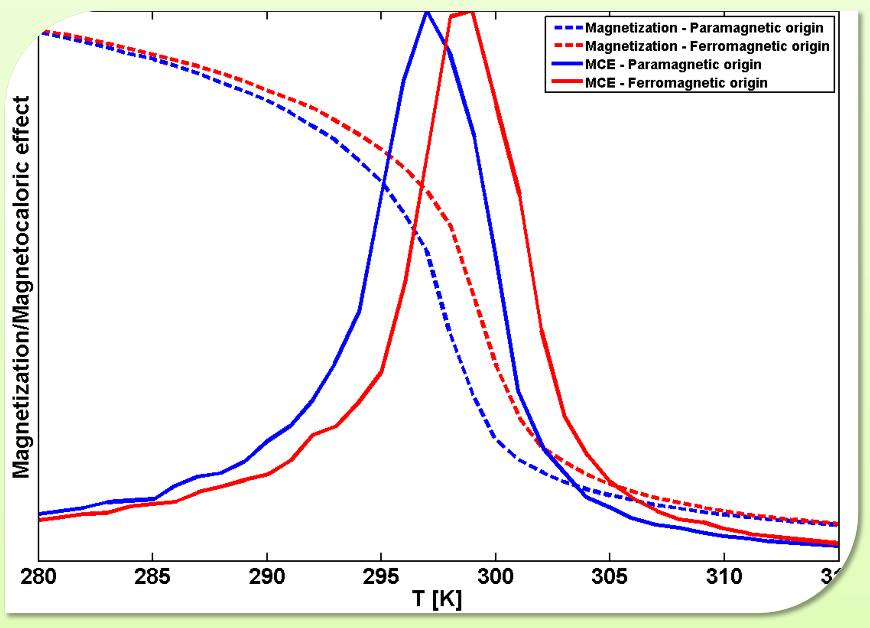
The field of magnetic refrigeration has grown a lot with the discovery of room temperature 1st order Magnetocaloric Materials (MCM), experiencing a large Magnetocaloric Effect (MCE). MCM are applied in Active Magnetic Regenerators (AMR), where they undergo thermodynamic cycles in order to heat or cool a system. This process has previously been modeled for 2nd order materials, but there is a general lack of detailed modeling of 1st order materials, where hysteresis is present [Nielsen et al.,2011].

We investigate how thermal hysteresis affects the heat capacity of the 1st order material MnFe(P,As) under partial phase transitions through Differential Scanning Calorimetry (DSC) and compare to a Preisach-type model.

Magnetocaloric materials and magnetic refrigeration

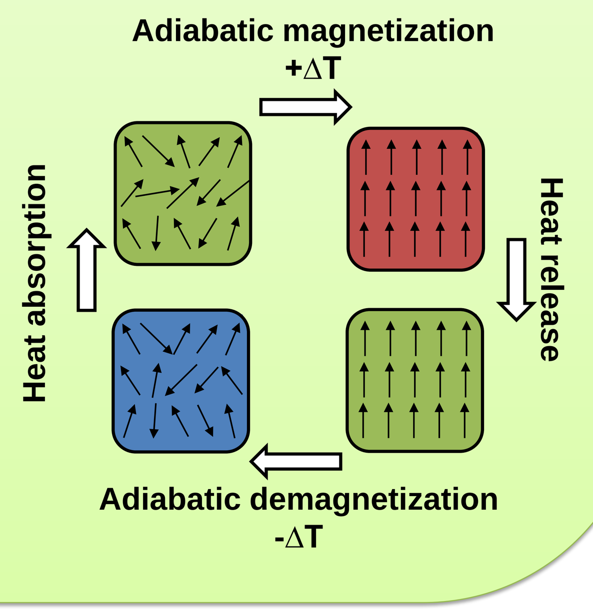
The magnetocaloric effect can be measured as the adiabatic temperature change in magnetic material when a magnetic field is applied. Under adiabatic conditions the total entropy remains constant and the decrease of magnetic entropy is balanced by an increase in lattice entropy and a temperature increase. See Smith et al., 2011 for a review.

$$\Delta T_{ad}(T,H) = -\int_{H_0}^{H_1} \frac{T}{c(T,H)}\bigg|_H \frac{\partial M(T,H)}{\partial T}\bigg|_H dH$$



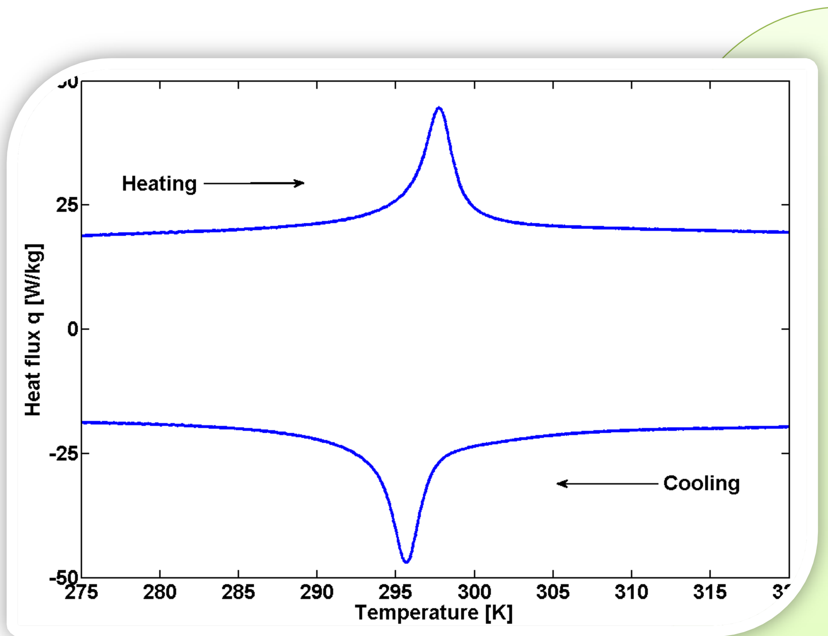
The magnetic refrigeration cycle

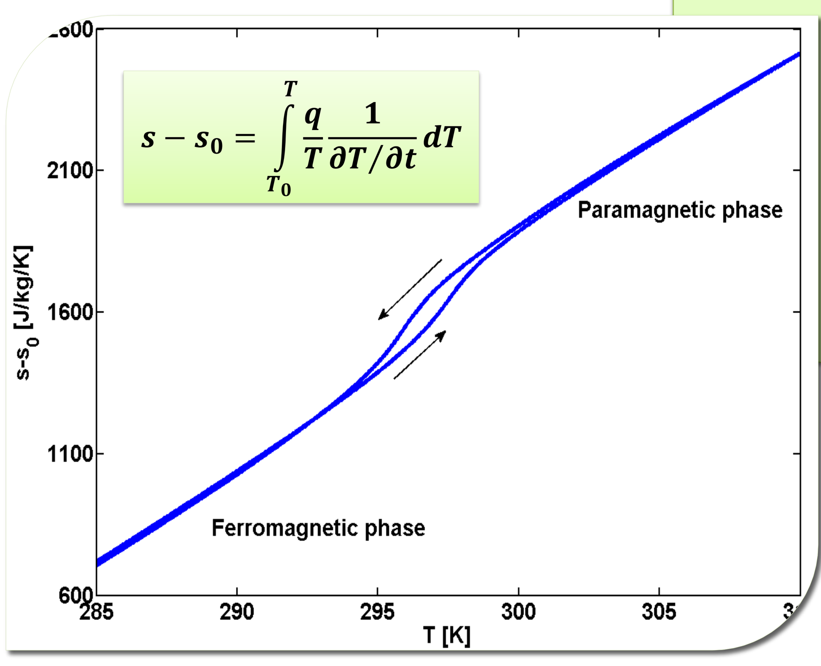
The MCE can be magnified by applying MCM in thermodynamic cycles, analogous to gas vapor-compression.



1st order materials

- Coupled structural and magnetic transition
- Large MCE! Wanted!
- Hysteresis… not wanted.





Material modeling

Setting the scale

The pure phase entropies are estimated through heat flux measurements, where the Gibbs free energies follow through $\partial g/\partial T = -s$.

Pure phase entropies are assumes linear

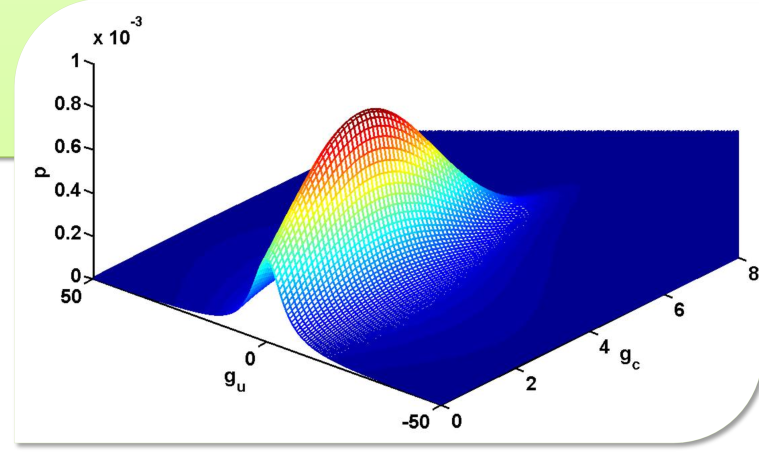
$$s_0(T) = c_b(T - T_{min}), \qquad s_1(T) = s_0(T) + \delta s$$

The right mix of hysteretic units

The Preisach distribution is assumed to have the form

$$p(g_u, g_c) \propto \frac{1}{1 + \left(\frac{g_u - g_{u,0}}{\sigma_u}\right)^2} \cdot \exp\left(-\frac{(g_c - g_{c,0})^2}{2\sigma_c^2}\right)$$

with $g_{u,0}$, $g_{c,0}$, σ_u and σ_c being material fitting parameters.



MnFe(P,As)

- 1st order material with a hexagonal Fe_2P structure.
- Phase transition between the low temperature ferromagnetic state and the high temperature paramagnetic state.
- The phase transition is magnetoelastic: at the transition temperature the c/a ratio of the hexagonal unit cell changes while the volume basically does not change [Dũng, 2012].

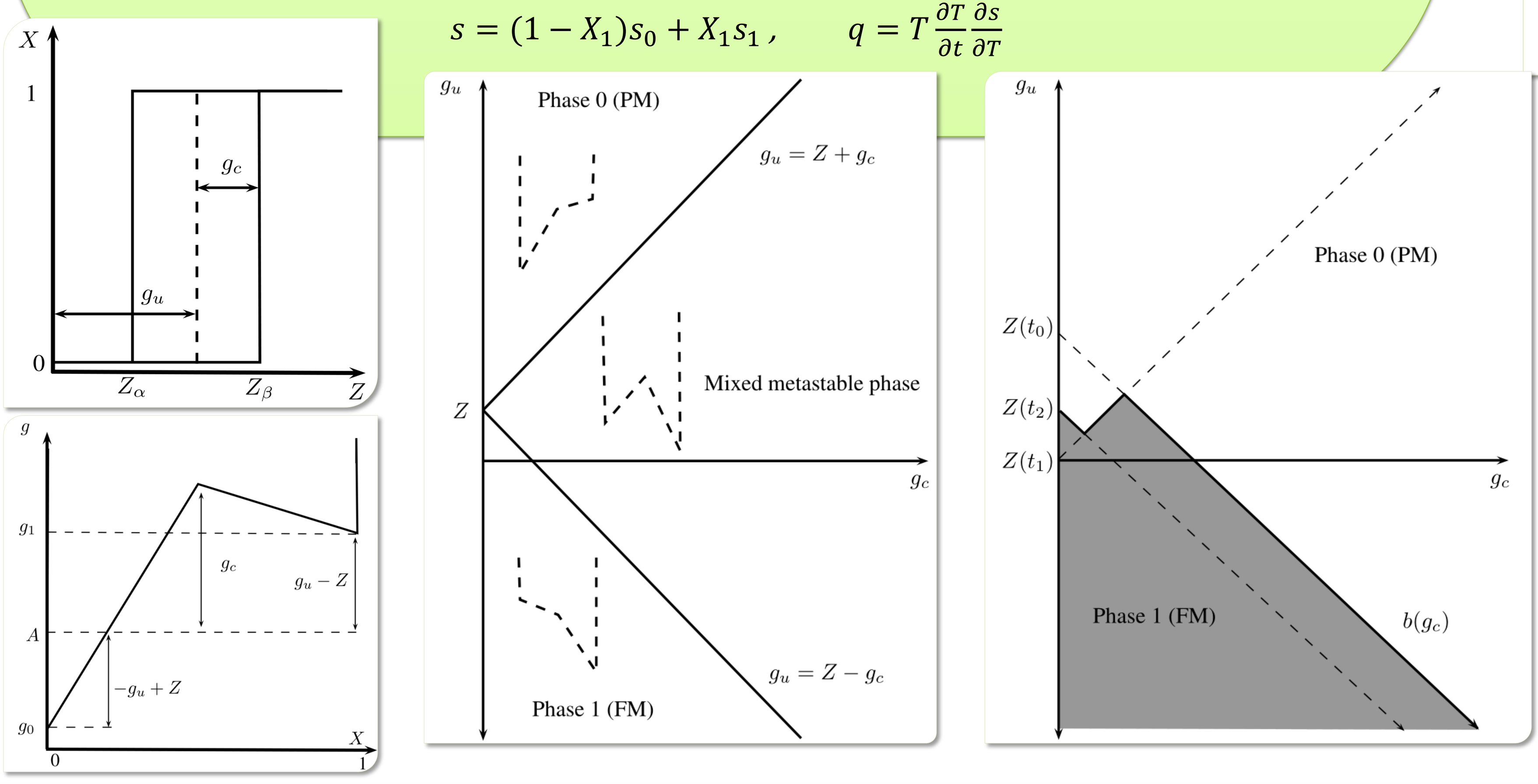
The Preisach-model

MCM behavior is often described by a set of *M(T,H)* and *c(T,H)* measurements. However, the applicability of such measurements in models is not straightforward when hysteresis is present.

Here we apply a Preisach-type model that is appropriate to describe the out-of-equilibrium thermodynamic aspects of hysteresis [Basso et al., 2007].

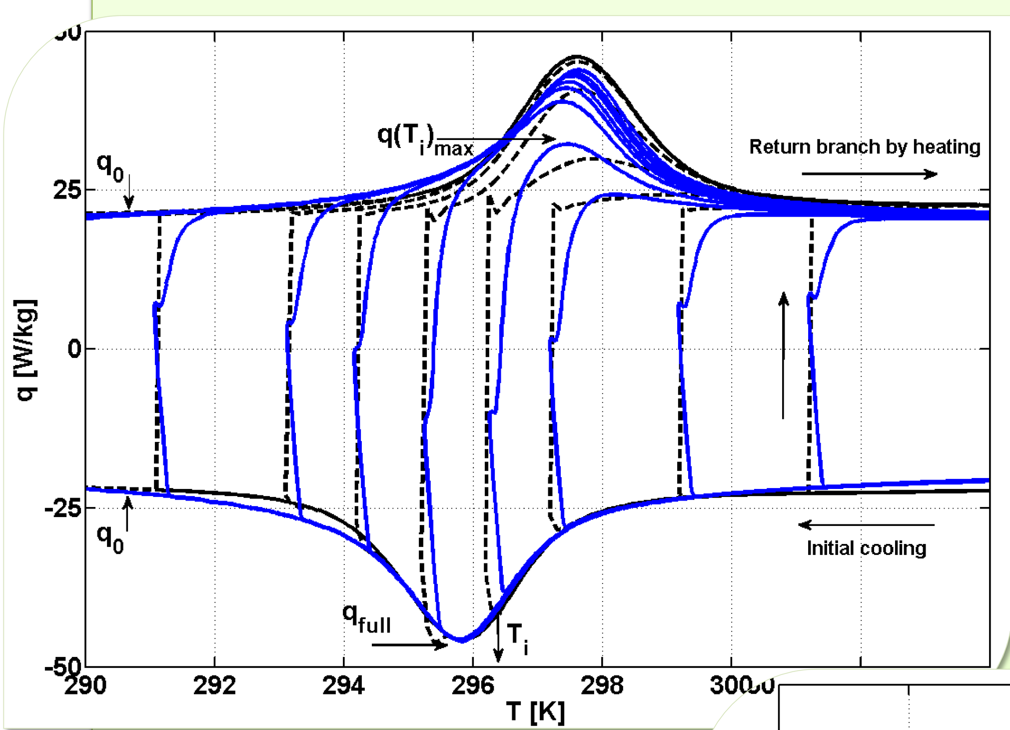
Modeling hysteretic behavior

- A distribution, $p(g_u, g_c)$, of bistable hysteretic units, which can be either in phase 1 (ferromagnetic) or 0 (paramagnetic).
- Each unit is represented by parameters (g_u, g_c) which determine the critical phase switching fields
$$Z_\alpha = g_u - g_c\,, \qquad Z_\beta = g_u + g_c$$
- The difference in the Gibbs potential between phase 0 and 1 is the driving force in the transition
$$Z(T,H) = \frac{g_0(T,H) - g_1(T,H)}{2}$$
- History of *Z*-field determines the transition line *b(g_c)*, which gives the current ferromagnetic phase fraction
$$X_1 = \int_0^{+\infty} dg_c \int_{-\infty}^{b(g_c)} p(g_u, g_c) dg_u$$
- The phase fraction gives the relevant thermodynamic quantities of the mixed phase state, utilizing the pure phase material properties, e.g. entropy and heat flux
$$s = (1 - X_1)s_0 + X_1 s_1\,, \qquad q = T\frac{\partial T}{\partial t}\frac{\partial s}{\partial T}$$



DSC measurements and model simulations

A 35 mg sample of MnFe(P,As) with T_C=296 K was measured with a commercial PerkinElmer Diamond DSC in 0 T magnetic field. The data is given as the heat flux *q* absorbed by the sample to maintain a constant temperature rate of ±2 K/min.

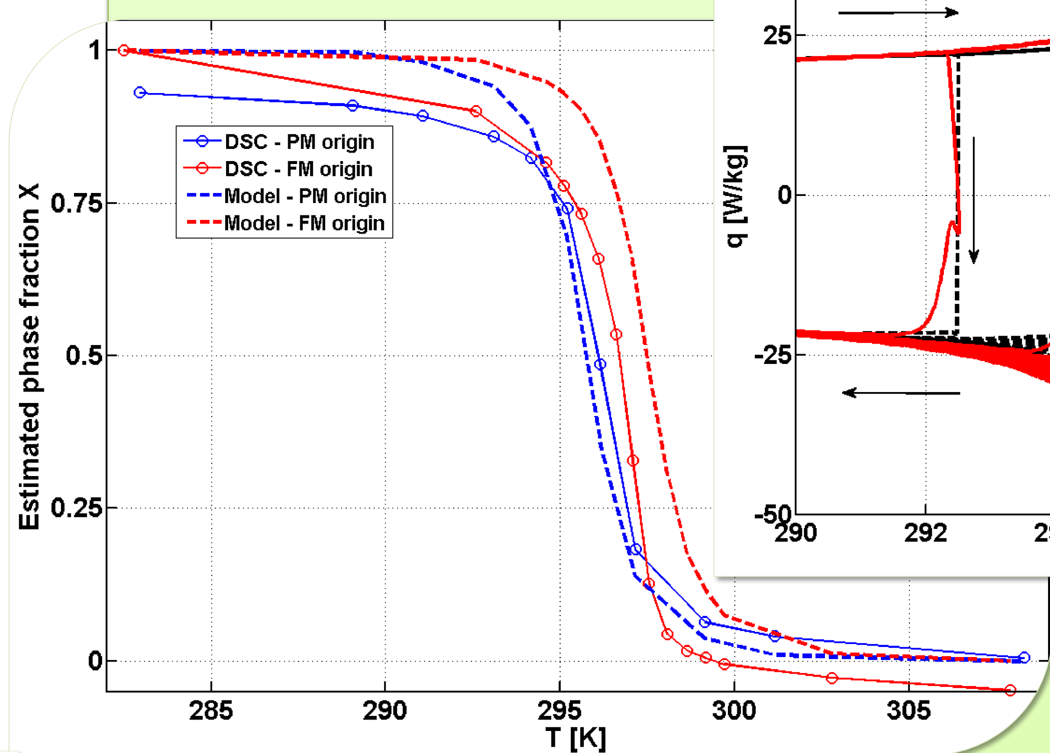


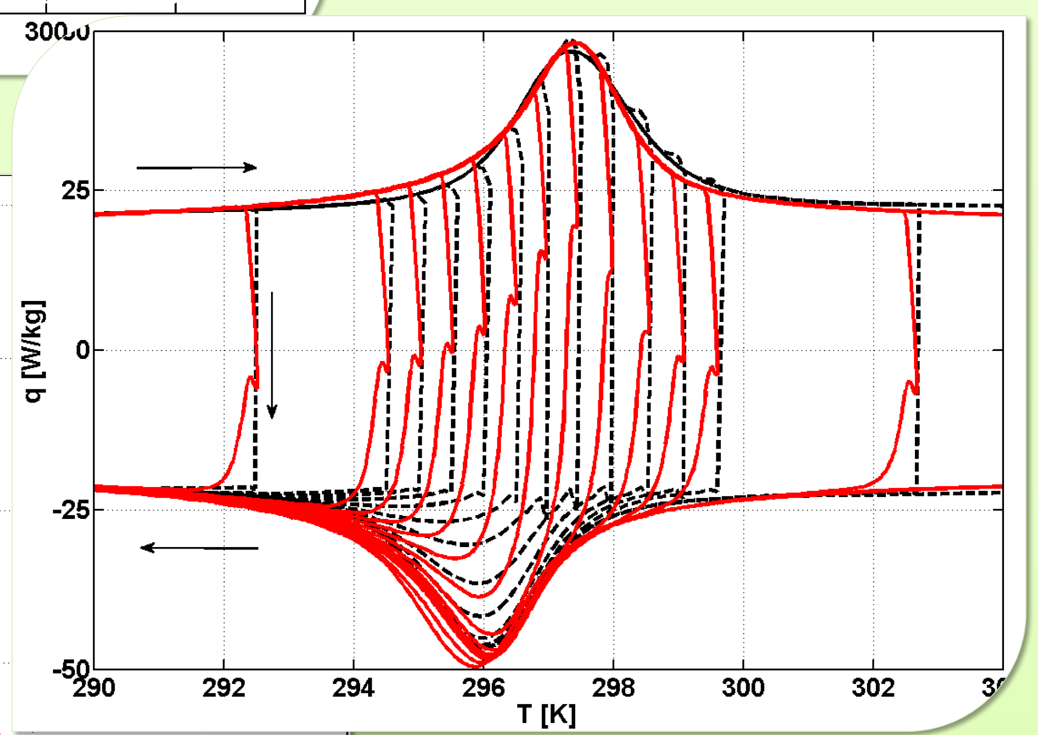
Measurements were performed with the sample originating in the PM phase (blue curve) and in the FM phase (red curve).

An estimated phase fraction is calculated from the data as

$$X_{est}(T_i) = \frac{|q(T_i)_{max}| - |q_0|}{|q_{full}| - |q_0|}$$

The experimental procedure was simulated with the Preisach model (dashed curves).





Results

- Model simulations fit well with complete transitions curves
- Model predictions of partial transitions lack detail and overestimate hysteresis → more detailed Preisach distribution
- Experimental data on partial phase transitions is needed to realistically model 1st order materials and the effect of hysteresis in AMR cycles

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